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(54) Title of the Invention: Polyester Resin Composition

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SPECIFICATION

1. Title of the Invention

Polyester Resin Composition

2. Claims

A polyester resin composition formed as a result of adding 0.05 to 10 parts by weight of a β -diketone with a molecular weight of 101 or more and less than 150 having the structural units of general formula (I), and/or a metal chelate thereof, per 100 parts by weight of thermoplastic polyester.



(In the formula, R_1 is a hydrocarbon group with a carbon number of 1 or more, and R_2 is a hydrocarbon group with a carbon number of 2 or more. R_1 and R_2 may form a ring structure.)

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a polyester resin composition that yields a molded article that can shorten the molding cycle in injection molding and has excellent solvent resistance.

(Prior Art)

Typical thermoplastic polyesters such as polyethylene terephthalate and polybutylene terephthalate have been rapidly receiving attention in recent years as engineering plastics because they have superior heat resistance, chemical resistance, mechanical properties, and other characteristics. Among these resins, polybutylene terephthalate has excellent moldability and is therefore used in increasing amounts in automotive components, electrical and electronic components, mechanical components, and other parts.

Nevertheless, even polyester, which has such excellent characteristics, has drawbacks in that polyethylene terephthalate, polybutylene terephthalate, and other polyesters have a prolonged molding cycle, require the use of high-temperature molds, and have other problems caused as a result of a low crystallization velocity, and these polyesters are currently not widely applied in injection molding. Even in the case of polybutylene terephthalate, which has a high crystallization velocity, further improvement is needed in the crystallization velocity in order to shorten the molding cycle and to improve productivity.

In order to improve such crystallization velocities, methods in which talc and other inorganic materials as well as higher fatty acid salts are added as nucleating agents have been studied. However, since the effect of improving the crystallinity of polyester is insufficient even if such nucleating agents are added, methods have been proposed whereby the acetylacetone metal salts disclosed in JP (Kokai) Nos. 56-41247, 57-14644, and other publications; the alkaline metal salts of dehydroacetic acid disclosed in JP (Kokai) 63-15840; or other substances are added as nucleating agents.

(Problems to Be Solved by the Invention)

However, when these methods are used to improve the crystallinity of polyester, there are drawbacks in that the molding cycle cannot be shortened when low-temperature molds are used for molding, and high-temperature molds must be used when the molding cycle must be shortened.

(Means Used to Solve the Above-Mentioned Problems)

In view of the above, the present inventors, as a result of thoroughgoing research aimed at obtaining a crystallinity improver that allows the molding cycle to be shortened in a low-temperature mold, arrived at the present invention having discovered that when a β -diketone having a specific structure and molecular weight, and/or a metal chelate thereof, is added to polyester, the initial problems are solved and the solvent resistance of the resulting molded article is excellent.

More specifically, the present invention provides a polyester resin composition formed as a result of adding 0.05 to 10 parts by weight of a β -diketone with a molecular weight of 101 or more and less than 150 having the structural units of general formula (I), and/or a metal chelate thereof, per 100 parts by weight of thermoplastic polyester.



(In the formula, R_1 is a hydrocarbon group with a carbon number of 1 or more, and R_2 is a hydrocarbon group with a carbon number of 2 or more. R_1 and R_2 may form a ring structure.)

The thermoplastic polyester used in the present invention is a polymer or copolymer obtained as a result of a polycondensation reaction in which the main components are a dicarboxylic acid (or an ester-forming derivative thereof) and a diol (or an ester-forming derivative thereof).

acid, 2,6-anthracene dicarboxylic acid, 4,4"-p-terphenylene dicarboxylic acid, and 2,5-pyridine dicarboxylic acid; and preferable among these is terephthalic acid.

Two or more of these dicarboxylic acids may be mixed and used together. It should be noted that in addition to these dicarboxylic acids, one or more of the following may be mixed and used in small amounts: aliphatic dicarboxylic acids such as adipic acid, azelaic acid, dodecanedioic acid, and sebacic acid; and cycloaliphatic dicarboxylic acids such as cyclohexane dicarboxylic acid.

Examples of the diol component include ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, neopentyl glycol, 2-methyl-1,3-propane diol, diethylene glycol, triethylene glycol, and other aliphatic diols; 1,4-cyclohexane dimethanol, and other cyclo-aliphatic diols; and mixtures thereof. One or more of the following with a molecular weight of 400 to 6,000 may be copolymerized as long as they are used in a small amount: polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and other long-chain diols.

Specific examples of the polyester include polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polycyclohexane dimethylene terephthalate, polyethylene naphthalate, polybutylene naphthalate, and polyethylene-1,2-bis(phenoxy) ethane-4',4"-dicarboxylate, as well as copolymers such as polyethylene terephthalate/isophthalate, polybutylene terephthalate/isophthalate, and polybutylene terephthalate/decane dicarboxylate. Preferred among these are polybutylene terephthalate, polycyclohexane dimethylene terephthalate, polyethylene naphthalate, and polyethylene terephthalate, which have a good balance between mechanical properties and moldability.

The polyester used in the present invention has an intrinsic viscosity of 0.25 to 3.0 dL/g, and preferably 0.4 to 2.25 dL/g, when measured at a temperature of 25°C in an o-chlorophenol solution.

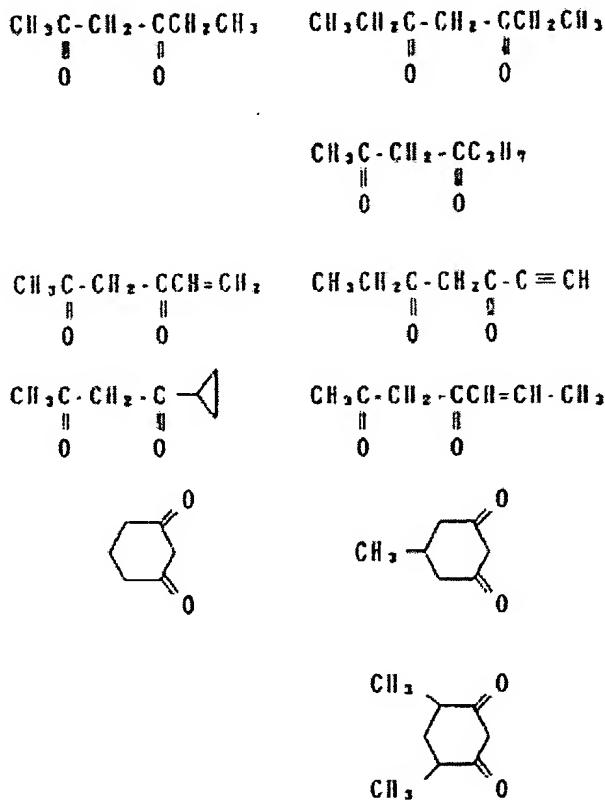
The β -diketones used in the present invention are not particularly limited as long as they have the structural units of general formula (I) and a molecular weight of 101 or more and less than 150, but preferred are those that have at least one unsaturated bond in the molecule, and more preferred at those that have an unsaturated bond that conjugates with at least one carbonyl carbon of a β -diketone, or those in which R₁ and R₂ have a ring structure. It should be noted that the chemical structure of the β -diketones is always referred to in the present invention as a keto

structure, but the structure may also be a compound described as a corresponding ethanol structure.

Specific examples of R_1 in general formula (I) include methyl, ethyl, propyl, vinyl, cyclopropyl, and other hydrocarbon groups; and specific examples of R_2 include ethyl, propyl, butyl, vinyl, cyclopropyl, and other hydrocarbons. Examples of groups when R_1 and R_2 bond to form a ring structure include trimethylene, tetramethylene, and pentamethylene.

The molecular weight of the β -diketone compounds used in the present invention is preferably 101 or more but less than 150. When the molecular weight is less than 100 (or when the carbon number of R_2 is less than 2 in general formula (I)), the amount of gas generated during molding is high, and when the molecular weight exceeds 150, the solvent resistance is often reduced, and both of these cases are accordingly not preferred.

Specific examples of the β -diketones used in the present invention include the following compounds.



Examples of the metals in the metal chelates of the β -diketones of the present invention include lithium, sodium, potassium, cesium, rubidium, barium, strontium, calcium, magnesium, titanium, iron, and the like. Among these, sodium, potassium, and lithium are preferred.

In the present invention, the β -diketone and/or metal chelate thereof may be used alone, or two or more types may be used together.

The addition amount of the β -diketone having the structural units of general formula (I) and a molecular weight of 101 or more but less than 150 according to the present invention, and/or metal chelate thereof, is 0.005 to 10 parts by weight, is preferably 0.01 to 5 parts by weight, and is more preferably 0.05 to 5 parts by weight, per 100 parts by weight of the thermoplastic polyester. If the addition amount is less than 0.005 parts by weight, the effect of improving the crystallinity of the polyester is not sufficient, and if the addition amount exceeds 10 parts by weight, the molecular weight of the polyester during manufacture of the polyester resin composition decreases, and the dynamic properties of the molded article tend to be compromised, and both cases are accordingly not preferred.

From the viewpoint of improving moldability, the composition of the present invention is preferably jointly used as required with organic acid salts or inorganic compounds. Specific examples of such compounds include sodium stearate, barium stearate, sodium salts or barium salts of partially saponified montanic acid esters, ionomers, sodium salts of phenols such as nitrophenol and formyl phenol, and talc.

Furthermore, the moldability can be further improved with the help of a method in which a compound known as a crystallization promoter and used in thermoplastic polyesters such as polyethylene terephthalate is added to the composition of the present invention. Specific examples of such crystallization promoters include polyethylene glycol, polypropylene glycol, and other polyalkylene glycols or carboxylic acid diesters thereof; α, ω -dialkyl etherified polyethylene glycols, α, ω -dialkyl etherified polypropylene glycols, and other α, ω -dialkyl etherified polyalkylene glycols; neopentyl glycol dibenzoate and other benzoic acid esters; and polylactone, polyethylene adipate, and other aliphatic polyesters.

It should be noted that as a result of further adding fibrous and/or granular fillers to the composition of the present invention, the rigidity can be considerably improved without compromising other physical properties, although this is not essential. Examples of such fillers include glass fibers, carbon fibers, metal fibers, aramid fibers, asbestos, potassium titanate whiskers, wollastonite, glass flakes, glass beads, talc, mica, clay, calcium carbonate, barium sulfate, titanium oxide, and aluminum oxide. Preferably used among these are chopped strand

types of glass fiber, talc, and titanium oxide. The amount of the fillers added is ordinarily equal to or less than 120 parts by weight per 100 parts by weight of the polyesters.

One or more of ordinary additives such as antioxidants, thermostabilizers, UV absorbers, lubricants, mold release agents, and colorants, including dyes and pigments, may be added to the composition of the present invention in a range that does not compromise the object of the present invention.

A small amount of thermoplastic resin (examples of which include polycarbonate, polyphenylene ether, polyamide, polypropylene, polyethylene, ionomer, ethylene/propylene copolymer, ethylene/butene-1 copolymer, ethylene/propylene/non-conjugated diene copolymer, ethylene/ethyl acrylate copolymer, ethylene/glycidyl methacrylate copolymer, ethylene/vinyl acetate/glycidyl methacrylate copolymer, and ethylene/propylene-g-maleic anhydride copolymer) may also be added.

The method of producing the composition of the present invention is not particularly limited, but examples of preferably used methods include a method in which both a thermoplastic polyester and a β -diketone, and/or a metal chelate thereof, are melted and mixed using an extruder, and a method for adding a β -diketone compound or a metal chelate thereof in the final stage of polymerization of the polyester. When inorganic filler or another additive is added, the additive is preferably melted and blended in at the same time as the two components described above using an extruder.

The resin composition of the present invention can easily be molded by means of injection molding, extrusion molding, or another ordinary method, and the resulting molded article has high crystallinity and exhibits excellent properties.

Working Examples

The effect of the present invention is described in greater detail with working examples below. The intrinsic viscosities in the examples are values measured in an o-chlorophenol solution at 25°C, and the parts and percentages are both based on weight.

Working Examples 1 to 5 and Comparative Examples 1 to 5

Additives (A) to (G) described below were blended in the ratios shown in Table 1 based on 100 parts by weight of polyethylene terephthalate (PET) with an intrinsic viscosity of

0.83 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 280°C.

The pellets were dehumidified and dried at 160°C for 5 hours, and an ASTM-No. 1 dumbbell was molded by using a 2-ounce screw inline-type injection molding machine set to a temperature of 280°C, a mold clamping pressure of 75 tons, an injection time of 15 seconds, a cooling time of 20 seconds, an intermediate time of 5 seconds, (this is assumed to be the standard molding cycle) and a mold temperature of 90°C. The cooling time was then gradually shortened to obtain the shortest molding cycle in which a dumbbell can be formed without deformation.

The dumbbell obtained with a standard molding cycle was subsequently immersed for 10 days in a mixed solvent composed of nitrobenzene/decalin (1:1) at 80°C, and the solvent resistance was studied by comparing the shape.

The results of the above are shown in Table 1.

It is apparent from the results of Table 1 that the molding cycle can be shortened and that the resulting molded article has excellent solvent resistance.

Working Example 6 and Comparative Example 6

Additive (A) was blended in the ratios shown in Table 1 based on 100 parts by weight of polycyclohexane dimethylene terephthalate (PCT) with an intrinsic viscosity of 0.94 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 305°C.

Next, the resulting resin composition was formed into dumbbells, and the solvent resistance of the dumbbells obtained in a standard molding cycle and the shortest possible molding cycle at a mold temperature of 100°C using an injection molding machine set to 305°C was studied in the same manner as described in working example 1.

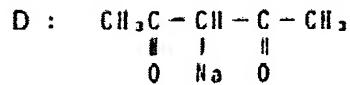
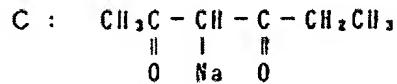
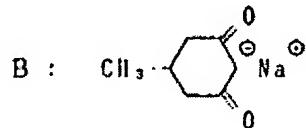
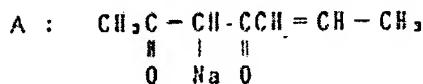
For comparative purposes, a test was carried out in the same manner for an example in which additive (D) was blended.

The results are shown in Table 1.

Table 1

Example	Base polymer (*)	Additive		Solvent resistance (Note:1)	Shortest molding cycle (seconds) (Note: 2)
		Type	Weight (parts)		
Working Example	1	PET	A	0.01	○
	2	PET	A	0.5	○
	3	PET	A	2.0	○
	4	PET	B	0.5	○
	5	PET	C	0.5	○
	6	PCT	A	0.5	○
Comparative Examples	1	PET	-	-	Not moldable
	2	PET	A	0.001	Not moldable
	3	PET	D	0.5	Δ
	4	PET	E	0.5	×
	5	PET	E	2.0	Δ
	6	PCT	D	0.5	Δ

* Additives



E: Sodium salt of dehydroacetic acid

(Note: 1): Solvent resistance

Dumbbells were immersed for 10 days in a mixed solvent composed of nitrobenzene/decalin (1:1) at 80°C, and the shape change was thereafter evaluated according to the following.

×: Marked deformation

Δ: Significant deformation

○: Almost no deformation

◎: No deformation at all

(Note: 2): Shortest molding cycle

Values indicate the cooling time, and a shorter time is better.

Working Examples 7 to 10 and Comparative Examples 6 to 8

Additives (A) to (F), and 30 parts of chopped-strand glass fiber (length: 3 mm, diameter: 11 μ) were blended in the ratios shown in Table 2 based on 100 parts by weight of polyethylene terephthalate with an intrinsic viscosity of 0.61 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 280°C.

The resulting polyethylene terephthalate composition was formed into dumbbells, the dumbbells molded in a standard molding cycle in the same manner as described in working example 1 were immersed for 10 days in a mixed solvent composed of nitrobenzene/decalin at 80°C, and the solvent resistance of the dumbbells was studied by measuring the percentage of weight loss after drying in a vacuum for 12 hours at 130°C.

The results of the above are shown in Table 2.

It is apparent from the results of Table 2 that the composition of the present invention has excellent solvent resistance even when glass fibers are present.

(Effect of the Invention)

Since the molding cycle at low temperature can be shorten, the polyester resin composition of the present invention has good productivity in injection molding and other molding methods, and since the solvent resistance is excellent, the composition can be used as electrical and electronics components, automotive components, mechanical components, and other parts.

Table 2

Example	Working Examples	Additive		Solvent resistance (Note: 4) (%)
		Type	Weight (parts)	
Comparative Examples	7	A	0.5	0.8
	8	B	0.5	0.1
	9	C	0.5	1.9
Comparative Examples	7	-	-	9.5
	8	D	0.5	6.2
	9	E	0.3	5.3

* Additives: Same as Table 1

(Note: 4): The weight reduction when the dumbbells were immersed for 10 days in a mixed solvent composed of nitrobenzene and decalin at 80°C, and a lower value is better.